

Surface Chemical Shifts by XPS

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CEM 924
April 27, 2001**

INTRODUCTION

X-ray photoemission spectroscopy (XPS) is a surface sensitive technique used to determine atomic compositions and learn information about the types of bonding that occurs within various compounds. Through the use of the photoelectron effect, as outlined by Einstein in 1905, spectra are resolved to paint a picture of what the surface looks like. Using an x-ray source, photons are created which have the ability to transfer their entire energy to electrons within atoms by striking them. If the energy transfer is sufficient, the receiving electron is jettisoned out of its energy level and away from the atom becoming a photoelectron. XPS works by sending massive amounts of photons toward the sample to produce large numbers of photoelectrons and comparing the kinetic energy with the initial energy of the photon. The difference is accounted for by the amount of attraction the electron has with the nucleus to remove it (binding energy) and the amount of energy the particle loses in transit from the sample to the analyzer (work function). While the work function is consistent for each sample on a specific XPS analyzer, the binding energy is dependent on the type of atom the electron came from as well as the environment it came from. The electrons of atoms that are photoemitted remain within a range of binding energies to help identify the specific element within the sample. Different types of bonds affect where in the range these binding energies fall creating a “chemical shift” which acts as another part of the compound’s fingerprint. For instance, a carbon of a carboxyl group will behave slightly different than that of a carbon in a methyl group. Comparing results of an unknown sample to those of other known standards leads to the identification of the compound or at least an idea of what sort of structure is present.

To say that all XPS analysis is strictly surface analysis is a bit of a misnomer however. Typical XPS analysis uses an incidence angle normal to the sample surface. Photons emitted from the x-ray source are then able to penetrate into the sample further than merely the top layer of atoms. Photoelectrons are then emitted from all of the atoms affected to create the subsequent spectrum. Since the atoms beneath the surface of the sample significantly outnumber the interfacial atoms, the majority of the signal comes from the interior. In fact, this analysis reflects what is present at 5 to 20 angstroms below the interface of the sample with the surrounding environment while barely noticing what falls outside of this range (Barr, 284-5). This gives more of a bulk feel to the information instead of truly revealing what is on the top layer of the

compound. Over the next few pages, this report describes what techniques are implemented in order to increase the surface sensitivity and the phenomena that are noticed when doing so.

SUMMARY OF THE TECHNIQUE

In order to discern more clearly between the surface and bulk photoelectrons that are emitted, it is necessary to alter the XPS technique. As stated earlier, typical XPS analysis is done from an incidence angle normal to the sample surface which allows for too much photon penetration and subsequently, too many photoelectrons from the bulk. By altering the angle of incidence, it is possible to change the sampling depth to a level that includes almost exclusively the surface atoms. While the bulk contribution to the signal is still present, the surface portion shows a significant boost in signal strength. The increase in surface resolution leads to analysis that can show a difference between binding energies of the surface atoms and the bulk atoms. This difference is known as a surface core-level shift (SCLS) and can be used to gain more information about the atoms at the interface as is discussed in the next section. Figure 1 demonstrates how the relative intensity increases for the surface contribution as the incident angle increases.

In order for this technique to be successful, there are a number of requirements that must be met. As in XPS, experiments are carried out under UHV ($\sim 10^{-9}$ torr or lower) to reduce the amount of noise in the spectrum and to avoid any extra peaks from contaminant atoms. Photons are also monochromated to avoid “ghost” peaks that make it impossible to discern surface and bulk contributions. This is usually done with a concentric hemispherical analyzer (CHA) in smaller labs or through the use of a synchrotron (an electron accelerator with a diameter of 20 to 30 meters) at research complexes. The preference seems to be for synchrotron photons because of its ability to be tuned to different energies and because of its presence in the literature (for example: Paolucci, 1990; Jacobi, et al. 1999; Jordan et al. 2000). It is also necessary to have high energy resolution in order to detect differences between surface and bulk contributions that are statistically significant (Citrin et al. p. 3161). SCLS values can be on the order of 0.1 eV which, with poor resolution, will appear to be noise statistically without confidence that the resulting binding energies are accurate.

The next step in analyzing these surface shifts, once accuracy is assured, is to parse the peaks that are produced on the XPS spectra. Using angle resolution, the shape of each peak can

change depending on the magnitude of the SCLS and the contributions of the surface and bulk atoms. With small incident photon energies, the bulk contribution is much less significant while large incident energies increase the bulk portion as seen in Figure 2. The data is assumed to be a combination of the bulk and surface contribution which leads to the creation of separate bulk and surface peaks to represent them. Each peak is fitted statistically fitted using lines of the Doniach- ν (DS) line shape that are dependent on two parameters: Γ and α (Doniach and ν , 1970) while the position of each peak depends on the average binding energy (i.e. the highest point of the peak) and the ratio of bulk to surface intensity (R). Γ represents the full width at half maximum (FWHM) Lorentzian lifetime, or in other words, how wide the peak should be which corresponds to the length of time the core hole is present. α has to do with the asymmetry of the peak itself, where an alpha of 0 would give a Gaussian curve and an alpha of 1 would skew the peak almost entirely to the left side of the maximum value. Then, the data is fit to two curves statistically, usually with a least-squares approach, to determine values for each of the parameters. This procedure is then repeated for each spectra of differing incident angle. Ideally, this should lead to accurate values for the binding energies of the bulk and surface atoms that are consistent across the range of angles. The difference between the two values then corresponds to the surface core-level shift of electrons at that particular level (Citrin et al. 1983). It is important to note that experiments need to be analyzed *individually* to ensure that each parameter is consistent between spectra. This double-checks the accuracy of the equipment, or at least how consistent it is. Should there be a significant drop in binding energy of the bulk photoelectrons with an increase of incidence angle, that should raise a red flag and the experiments should be repeated.

EXAMPLES IN LITERATURE

Papers from Jordan et al. (1997, 2000) outline how SCLSs are used to identify electronic structure of sampled surfaces. The research focuses on samples of equi-atomic CuAuI to determine whether the compound is copper or gold terminated along the (001) surface. Using photon energies of 130 eV and resolving the incident angle of the photons, Jordan et al. developed a picture of the bulk and surface contributions to the spectrum. They chose the lower photon energy to lower the mean free path of the photoelectrons. With less kinetic energy, the

photoelectrons have a more difficult time escaping from the bulk of the sample leading to a much more surface sensitive technique. The increase of the incident angle also has the same effect by having the photoelectrons travel through each layer for larger amounts of time instead of travelling perpendicular to the surface. Taking two spectra of the same sample at two different incident angles then leads to the construction of theoretical bulk and surface contributions to determine binding energies of each. Comparing the two cases leads to a binding energy for the bulk and surface leading to a surface core-level shift between the surface and bulk atoms. Ideally, both cases at normal emission and the larger angle (60° in this example) should have the same binding energies for both the surface and the bulk. The difference between these two peaks then leads to the subsequent SCLSs.

Since the compound has a layered tetragonal structure, the planes normal to the (001) surface are alternating between Cu and Au. Theoretical charge transfers as well as SCLSs are calculated using molecular simulations to build a picture of what can be expected from the surface. Jordan found, through the testing, that if the surface layer showed negative shifts for gold that the outer layer was gold and thus terminated with Au atoms. If the copper SCLSs were negative, then copper terminated the compound. The 1997 paper outlined this conclusion while the 2000 paper outlines the experiment and shows data that supports the conclusions. Both papers combine to show how XPS can be used to find more information by using normal and grazing angles to find out more information about the sample.

A research group from Italy also used the angle resolved XPS to gain information about oxygen adsorption onto a ruthenium surface (Baraldi et al., 2000). Baraldi et al. used XPS to deduce adsorption sites of oxygen based on how the spectra reacted to different coverages. From LEED spectra, as seen in Figure 3, oxygen shows adsorption in $c(2 \times 4)$ and (2×1) pg configurations depending on oxygen coverage (Schwegmann et al., 1998). The O atoms show a $c(2 \times 4)$ bonding pattern up to 0.5 monolayer (ML) coverage and then reverts to the (2×1) pg form with additional oxygen. While this is a good starting point, there are many possibilities for the actual placement of each of the oxygen atoms as seen in Figure 4. The Baraldi group chose the ten most plausible schemes for the adatoms bonding to the ruthenium. With these in mind, they set about to find the correct adsorption scheme using XPS spectra.

Their first step involved observing the oxygen 1s peak and looking for significant shifts in the binding energy while dosing the sample with O_2 . Analysis shows that the core-level

binding energy shifts only 75 ± 10 meV which is not significant enough to suggest an adsorption scheme. It does suggest, however, that the oxygen atoms bonded to the surface do not move when shifting to the new configuration. Unfortunately, there are six possible types of binding sites which leads to the ten possibilities mentioned above. With another route of analysis necessary, the Baraldi group scrutinized the $3d_{5/2}$ electrons of the ruthenium surface.

Their initial XPS spectrum of the clean Ru surface produced a peak with a binding energy of about 280 eV with a couple of bumps on the lower energy side of it. These bumps come from the first and second layer contributions of the atoms and are effectively the surface core-level shifts. Again using the Doniach-ujji³ line shapes for modeling, Baraldi produced three peaks that represent the first layer, second layer, and bulk additions. The next spectrum looks at the sample after being dosed with oxygen to give a coverage of 0.5 ML. Predictably, the peak shape is different and again, the Italian group parsed the peak into three smaller contributions. The bulk and second layer peaks are consistent with the first sample. However, the first layer peak has disappeared suggesting that all first layer ruthenium atoms have been covered with an oxygen atom. Keeping this in mind, it effectively eliminates eight of the ten considered adsorption patterns because of their presence of uninhibited first layer Ru atoms. This leaves two bonding models where the oxygen adsorbs to three fold hexagonal close-packed (hcp) sites that yield an equal number of each type of ruthenium atom involved in the adsorptions (i.e. first layer Ru bonded with O and second layer ruthenium atoms). While it does not give the exact pattern of oxygen adsorption, it narrows the field down significantly and gives further insight to the structure of the Ru surface that was not previously known

CONCLUSIONS

Surface core-level shifts can be powerful indicators used with XPS that come with the same caveats as XPS along with some other considerations. For one, the equipment is very expensive (from \$150,000 - \$750,000). Stainless steel is used as the building material to reduce the amount of atmospheric molecules that are able to diffuse into the vacuum chamber. Ultra-high vacuum is necessary to get results without a large amount of noise in the spectra from contaminants. Monochromation of the x-ray source is a tedious and expensive process through the use of either of a concentric hemispherical analyzer or a synchrotron. Also, sample preparation can be quite time consuming. While the XPS scanning itself may take a matter of

minutes, ensuring a good sampling environment can take days with evacuation of the chamber, annealing and sputtering the sample, as well as other details such as plugging leaks to ensure a sufficient vacuum on the system. Care must be taken, as well, to ensure that the sample does not become charged due to the flux of electrons. The flux of electrons can cause a charge distribution on the sample if the material cannot distribute the electrons in such a manner to neutralize the surface. Most experiments use noble metals which are known for their conductive nature. Without conduction, the charges build up and make the subsequent spectra extremely complicated. One final point is that high accuracy is necessary in the equipment in order to properly evaluate SCLSs. Some core-level shifts are less than 0.1 eV which cannot be accurately assessed if the sensitivity of the equipment is not on that order of magnitude or less. Otherwise, the shift will be deemed statistically nonexistent and defeats the purpose of the technique.

Despite all of the pitfalls, the technique itself is very useful. XPS itself is a straightforward technique, even if the equipment is not; shine a light on the sample, catch the emitted photoelectrons, and compare their energy with that of the initial photons. In addition, XPS becomes truly surface sensitive with the addition of the angle resolution. With low photon energies in addition to the high incident angles, the spectrum primarily reflects what is in the first monolayer of the material instead of what lies beneath it. This increase in resolution gives insight on the actual electronic structure of the surface which yields helpful results that other techniques cannot produce as well or as easily. The produced data is also quite accurate, with resolution on the order of 0.1 eV, which helps to make the information reproducible. XPS is also very useful in conjunction with other techniques to fill in the entire picture of a surface. While EELS or STM may provide an idea of what the surface looks like physically, XPS shows what is binding to what. With depth profiling, that picture can be focused even more by showing what is directly beneath the first layer as well.

All being said, using surface core-level shifts as an analytical tool is a viable option if you can afford it. XPS spectra are information rich and give another dimension to any surface analysis. By making it surface sensitive, bulk and interfacial bonding information is gathered simultaneously, eliminating the need for another experiment and possibly another technique. The versatility and usefulness of XPS is why it will remain a technique of choice for years to come (Vickerman, 1997).

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